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14. ABSTRACT
This slide presentation summarizes the approach to be followed when evaluating the natural attenuation of MTBE and other fuel oxygenate and considers the consequences of the unique physical and chemical characteristics and their resultant behavior in the environment.

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MTBE, natural attenuation, fuel hydrocarbons, oxygenates, biodegradation, groundwater remediation, geochemistry, contaminant destruction rates

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Methyl Tertiary-Butyl Ether (MTBE) Its Movement and Fate in the Environment and Potential for Natural Attenuation

Parsons

Parsons Engineering Science, Inc.

and the

Air Force Center for Environmental Excellence

Air Force Center For Environmental Excellence

Talk Based on *MTBE – Its Movement and Fate in the Environment and Potential for Natural Attenuation*

Technical Summary Report Prepared for AFCEE

Presents results of a comprehensive literature review of case histories of the fate of MTBE in the environment, and evaluate its potential for natural attenuation.

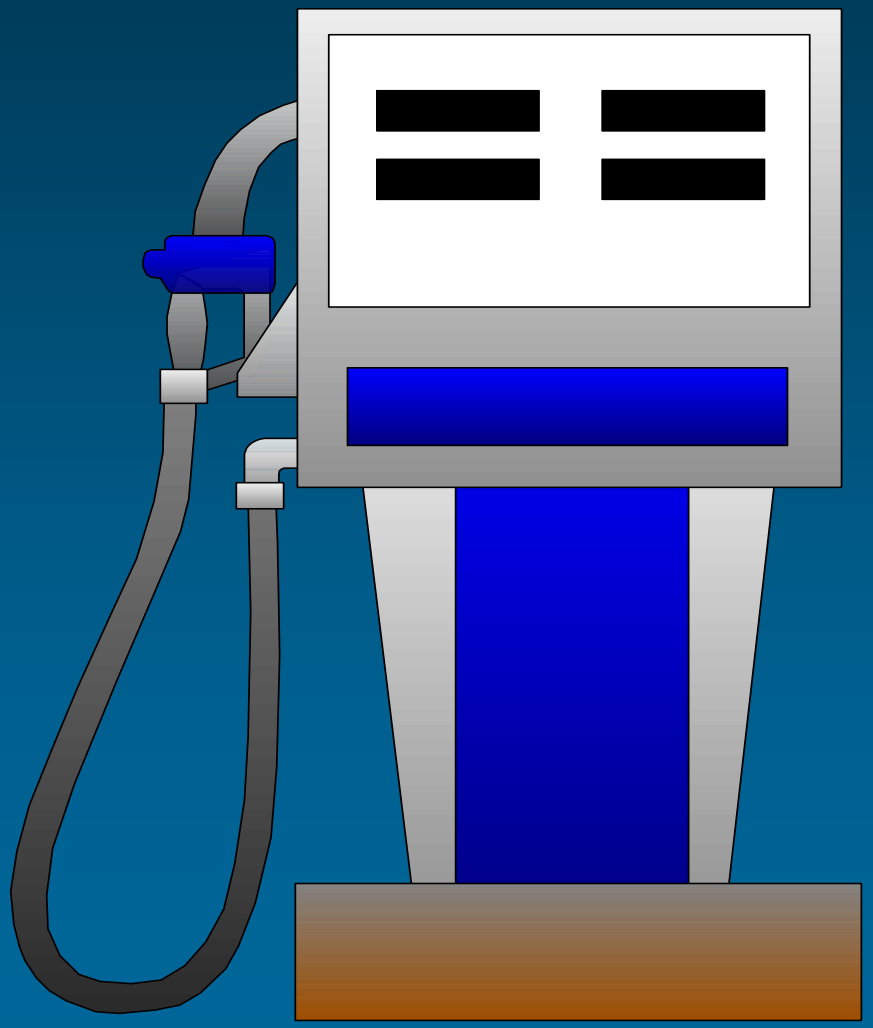
Presentation Outline

- **Introduction**
- **Properties of Methyl *tertiary*-Butyl Ether (MTBE), and its Movement and Fate in the Environment**
- **Natural Attenuation Potential**
- **Methodology to Evaluate Natural Attenuation**
- **Considerations and Recommendations**

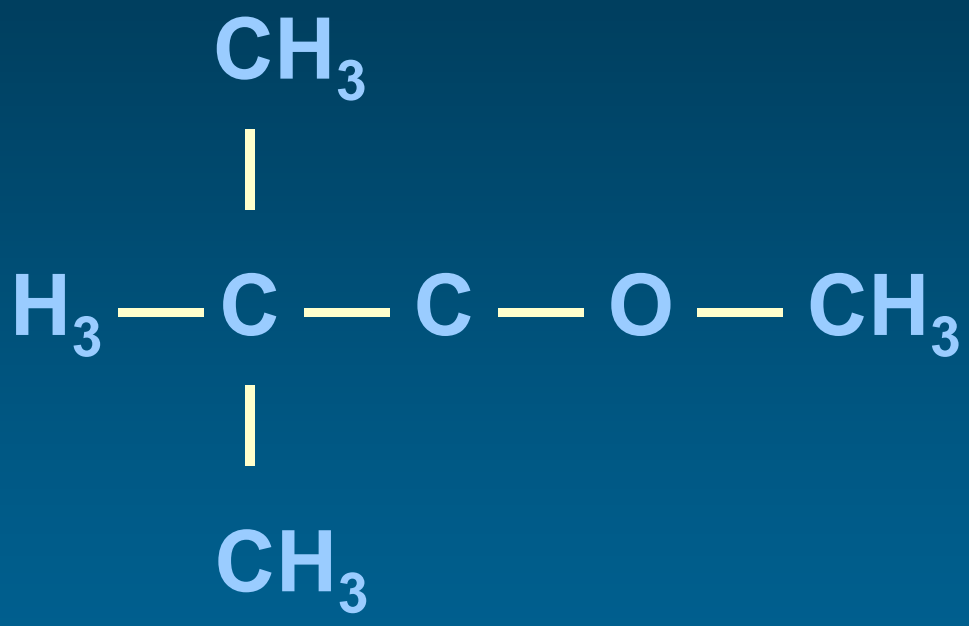
What is MTBE ?

What is MTBE ?

- **Gasoline Additive**
  - **Increases octane**
  - **Oxygenates fuel**



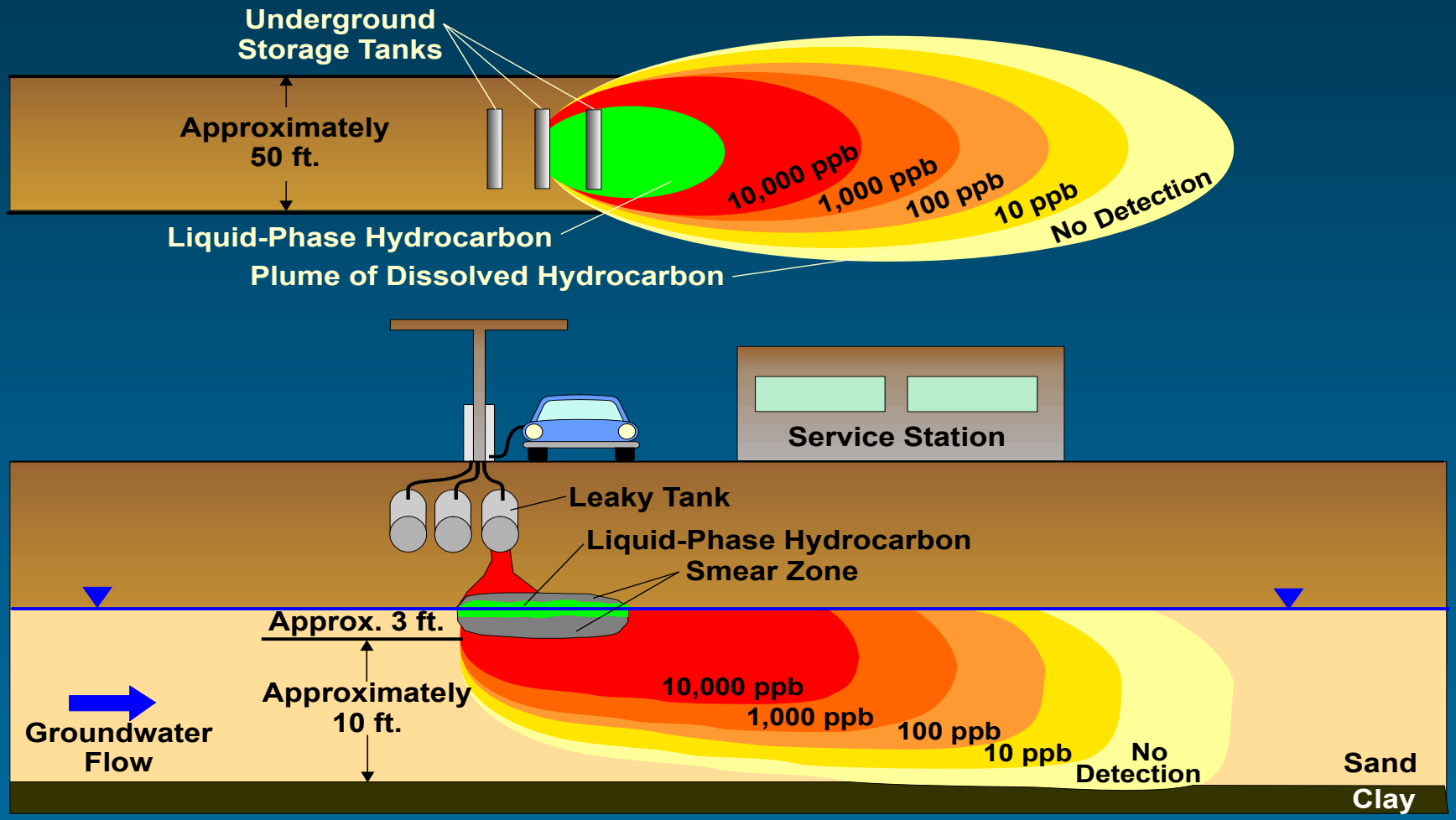
Chemical Structure



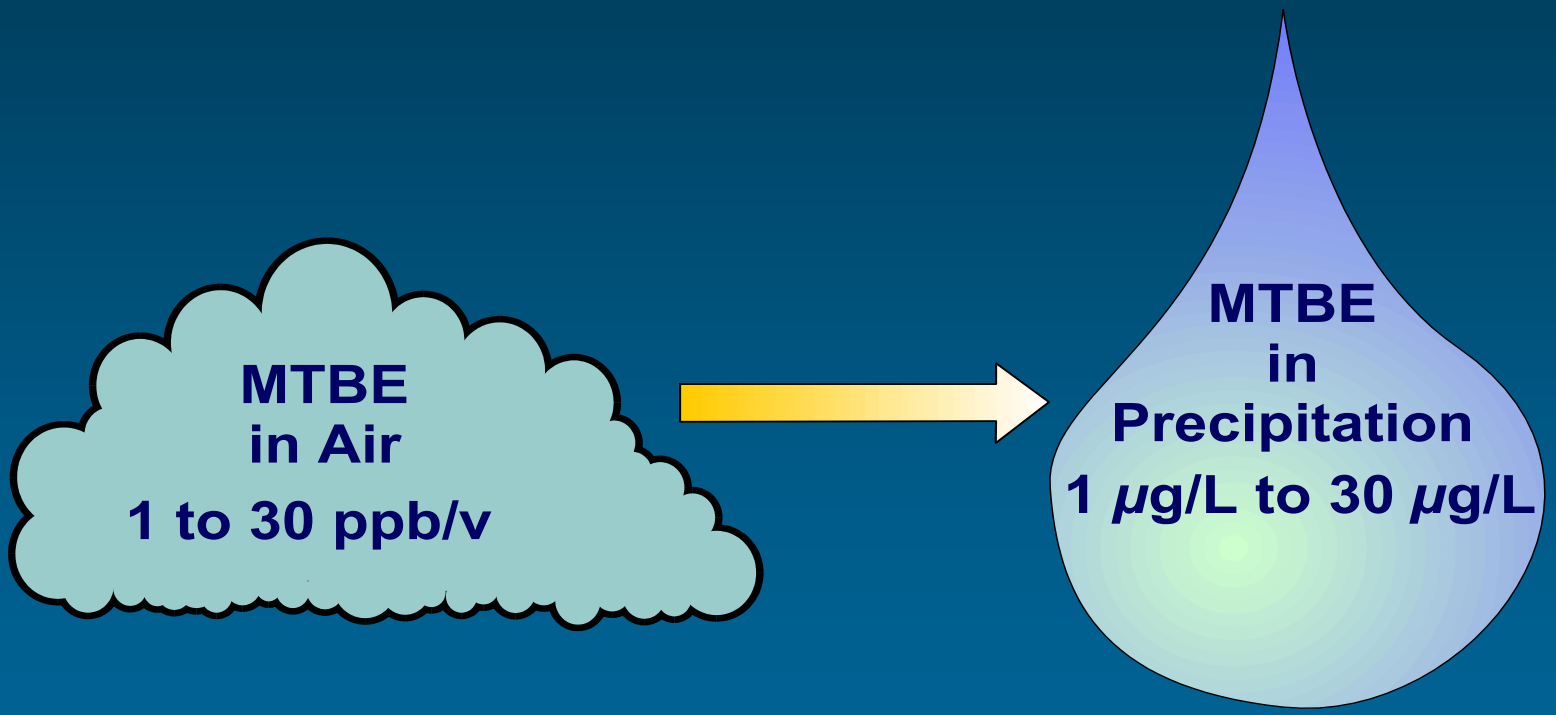
Sources of MTBE Contamination

- **Point Sources (UST leaks, fuel spills)**
  - **typically high concentrations**
  - **30 to 1,000,000 μg/L**
- **Non-point Sources (precipitation, runoff)**
  - **low concentrations**
  - **non-detect to 30 μg/L (typically < 5 μg/L)**

UST Leak and Dissolved Hydrocarbon Plume



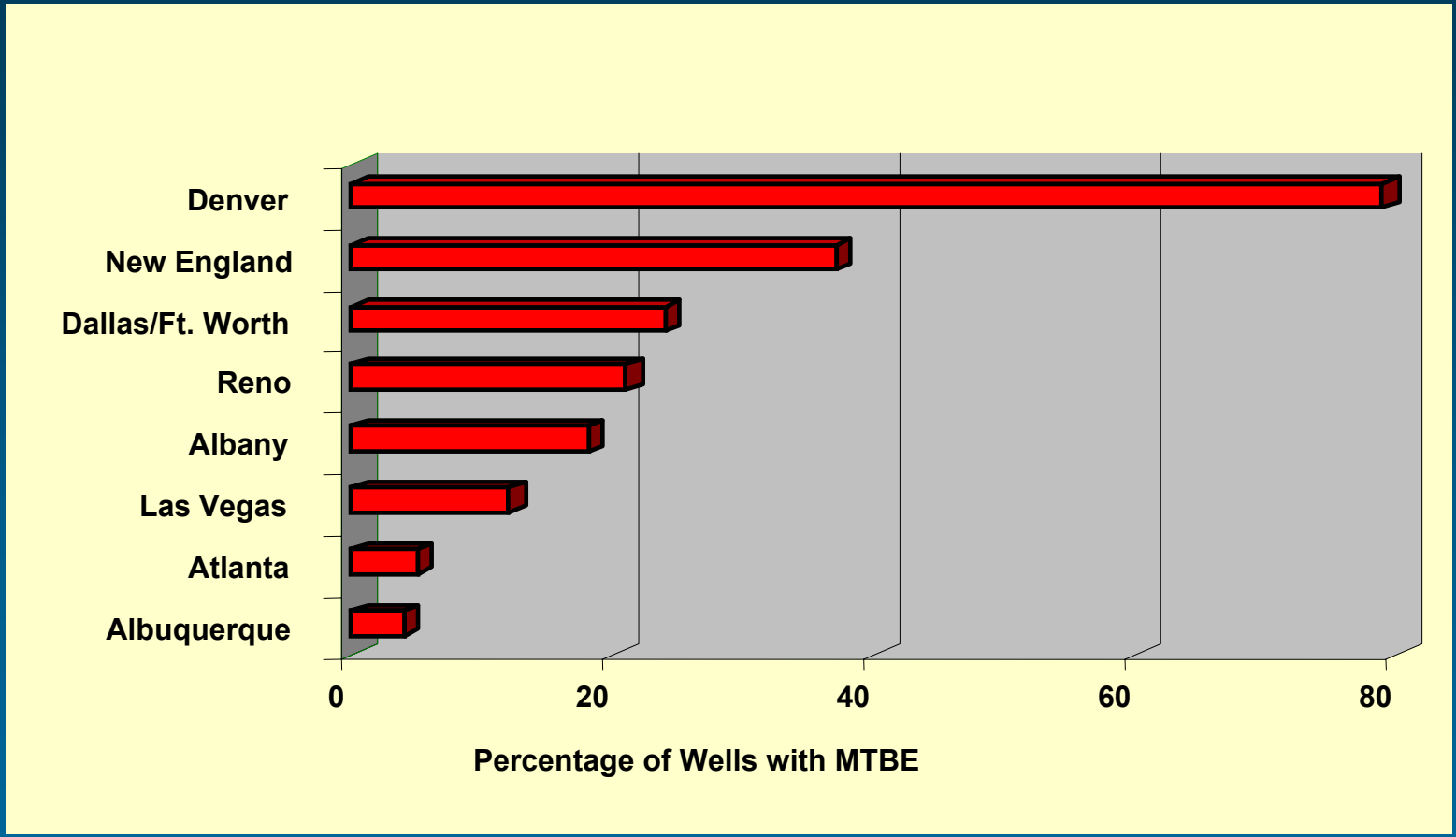
MTBE in Precipitation



USGS NWQA Program

- **Second Most Common VOC detected**
  - **210 urban wells sampled; 27% contained MTBE**
- **Concentrations**
  - **73% < 0.2 μg/L**
  - **24% from 0.2 to 20.0 μg/L**
  - **3% > 20.0 μg/L**

Frequency of MTBE Detection

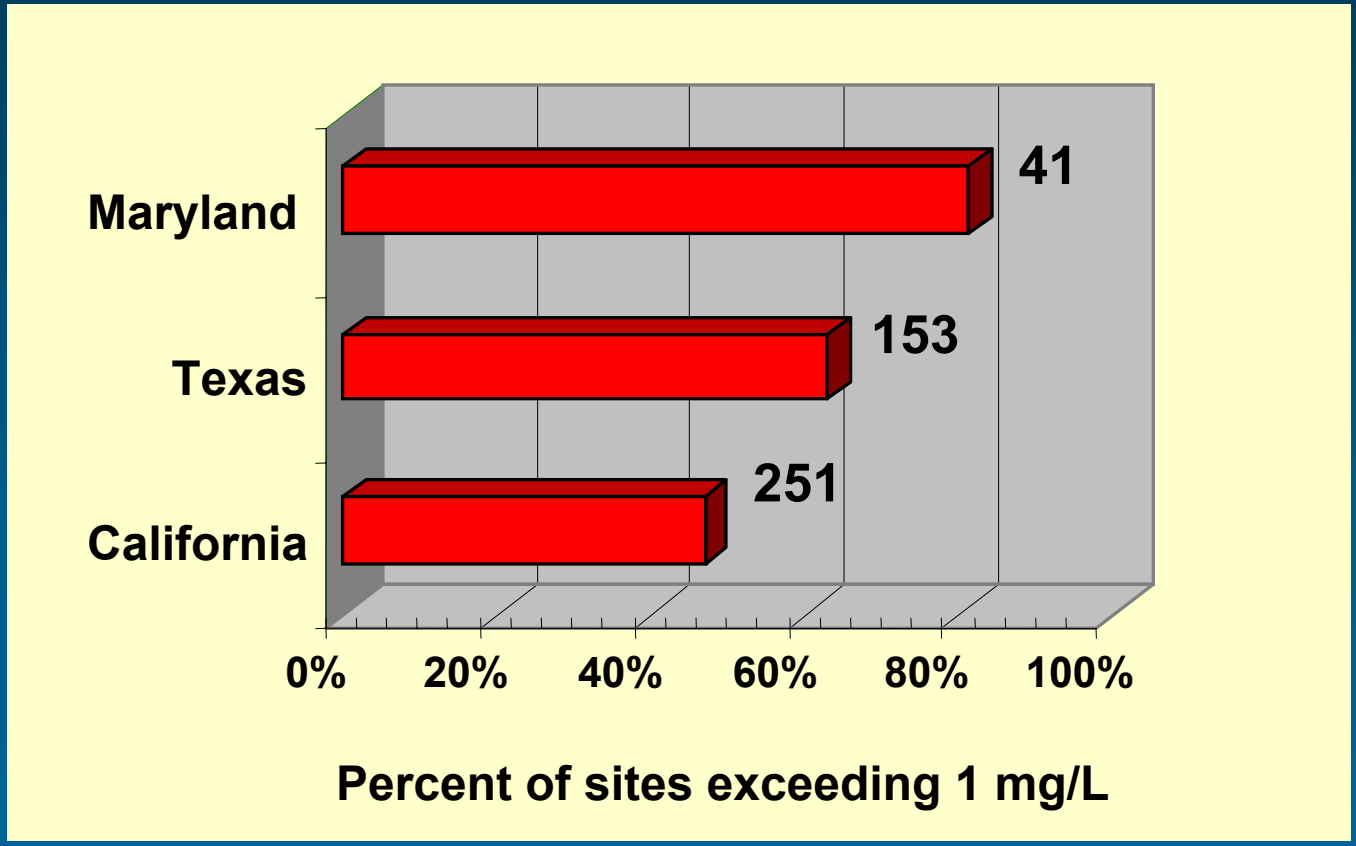


What petroleum products can contain MTBE?

- **Gasoline**
- **Aviation Fuel**
- **Jet Fuel**
- **Diesel**
- **Heating Oil**
- **Waste oil**

Source: Kostecki and Leonard (1998)

MTBE at UST Sites



T. Buscheck et al.,1998

Why is it a problem ?

- **Recalcitrant nature**
- **Increasing regulation**
- **Chemical properties**

Recalcitrant nature

- **Conditions that favor biodegradation not well understood**
- **Slow biodegradation to nonexistent**
- **Few research studies**

Increasing Regulation

- **USEPA Drinking Water Advisory**
  - **20 to 40 μg/L**
- **Standards in 25 States**
  - **Groundwater**
  - **Drinking water**
  - **Soil**

Chemical Properties

- **High Aqueous Solubility**
  - **50,000 mg/L (MTBE) vs. 1,780 mg/L (benzene)**
- **Low Koc**
  - **11.4 mL/g (MTBE) vs. 80 mL/g (benzene)**
- **Low Henry's Law Constant**
  - **~ 0.02 (MTBE) vs. 0.22 (benzene)**

Fate & Transport Mechanisms

- Advection
- Dispersion
- Sorption and Retardation
- Volatilization
- Biodegradation

Chemical Characteristics of MTBE that Affect its Movement and Fate in the Environment

- **Solubility**
- **Volatility**
- **Partitioning (fuel, air, water, sorbed phases)**

Compare MTBE with Benzene

- **Benzene**
  - **Typical contaminant of concern**
  - **MCL -- 5 µg/L**
  - **Known toxic effects (carcinogen)**
- **MTBE**
  - **Also often found associated with fuel spills**
  - **Safe Drinking Water Act Candidate List**
  - **Drinking-water advisory -- 20 - 40 µg/L**
  - **Standard based on taste & odor threshold**

Compare MTBE with Benzene

- **Vapor Pressure**
  - **MTBE = 200 mm Hg @ 20° C**
  - **Benzene = 76 mm Hg @ 20° C**

Conclusion:
MTBE more volatile from the chemical phase to the vapor phase.

Compare MTBE with Benzene

- **Aqueous Solubility of Pure Phase**
  - **50,000 mg/L (MTBE) vs. 1,800 mg/L (benzene)**

Conclusion:
MTBE is ~30 times more soluble than benzene

Effective Aqueous Solubility

$$S_i^e = \gamma_i \cdot X_i \cdot S_i^o$$

(describes dissolution of constituent from fuel)

$\gamma_i = 1.1$

X_i = mole fraction (≈ volume fraction)

$S_i^o \approx 50{,}000$ mg/L (solubility from pure phase)

$S_i^e \approx 5{,}000$ mg/L (MTBE; ~15% by volume)

$S_i^e \approx 50$ mg/L (benzene; ~3% by volume)

Fuel-Water Partition Coefficient

$$K_{fw} = \frac{\text{concentration in gasoline (mg/L)}}{\text{concentration in water (mg/L)}}$$

(describes tendency of a constituent to partition from fuel to water)

- MTBE $K_{fw} = 15.5$
- Benzene $K_{fw} = 350$

Conclusion:

MTBE partitions out of the fuel phase and into the aqueous phase much more readily than benzene

Henry's Law Constant

$$H = \frac{\text{concentration in air}}{\text{concentration in water}}$$

(describes tendency of constituent to partition between aqueous and vapor phases)

- **0.02 (MTBE) vs. 0.2 (benzene)**
- **MTBE is 10 times less volatile from aqueous phase**

Conclusion:

MTBE prefers the aqueous phase

Soil-Water Partition Coefficient

$$K_d = \frac{\text{sorbed concentration}}{\text{aqueous concentration}} = f_{oc} \times K_{oc}$$

(describes relative tendency of dissolved constituent to partition between the sorbed and aqueous phases; depends on fraction of organic carbon in soil [f_{oc}] and chemical organic-carbon partition coefficient [K_{oc}])

- **Koc = 11 mL/g (MTBE)**
- **Koc = 80 mL/g (benzene)**

Conclusion:
MTBE partitions to soil much less than does benzene

Retardation Factor

$$R = 1 + (\rho_b \times K_d)/ n$$

(ratio between migration velocity of dissolved constituent and groundwater flow velocity)

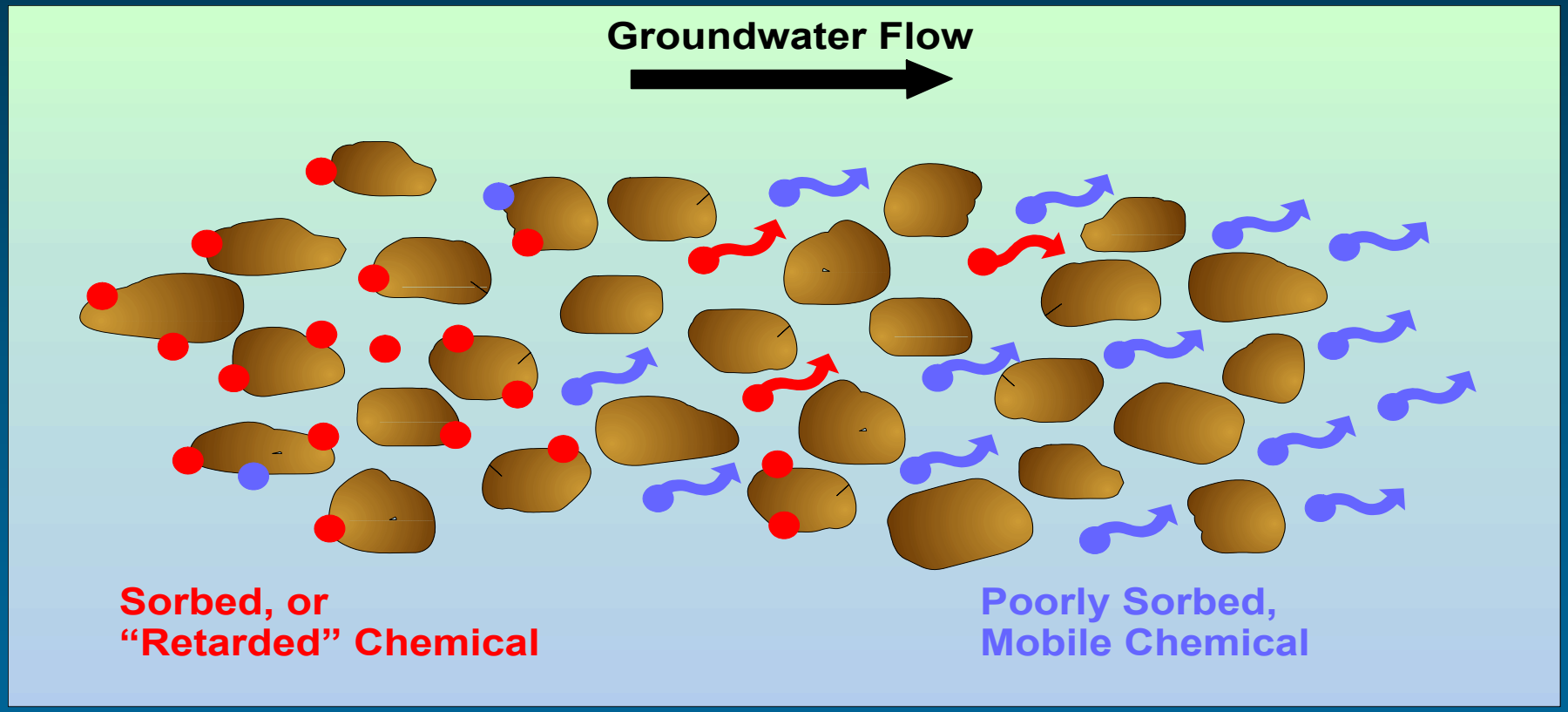
Representative Values of Retardation:

- **R = 1.05 (MTBE)**
- **R = 1.6 (benzene)**

Conclusion:

MTBE velocity ≈ groundwater velocity

Chemical Retardation and Dispersion



Bottom Line

- **MTBE is Much More Mobile and Persistent in Groundwater than BTEX**

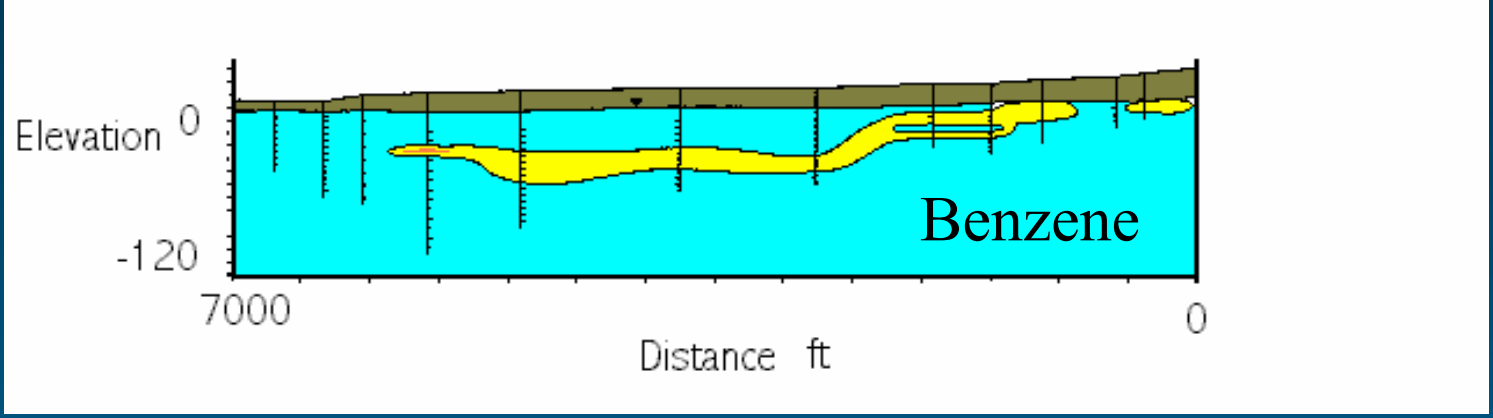
- **MTBE Tends to Leach out of Source Areas Faster than BTEX, thus it will Leave the Source Area Sooner**

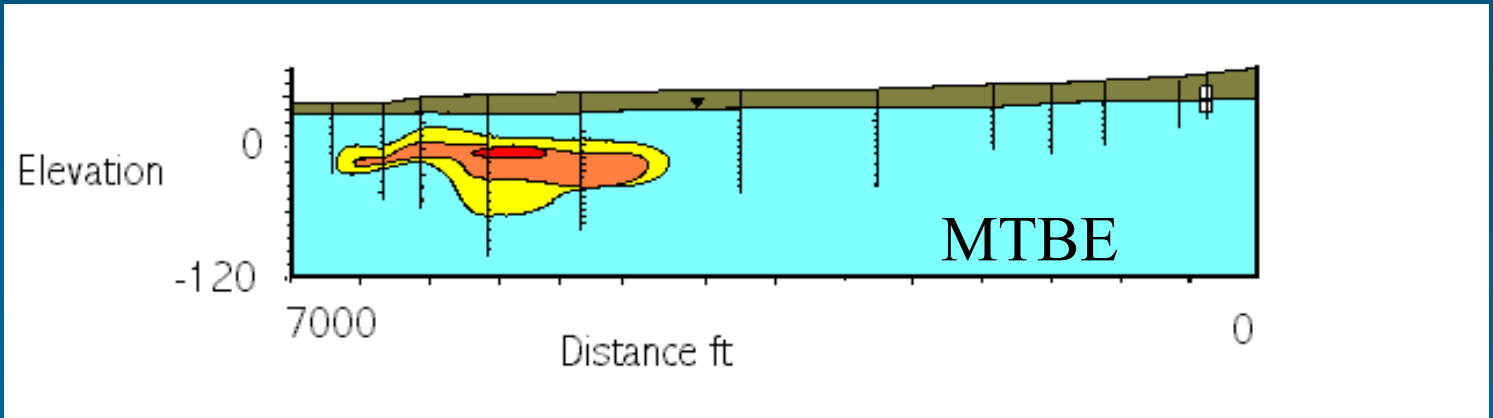
Example of MTBE Fate & Transport

- **East Patchogue NY, gasoline spill ***
  - **USEPA site**
  - **3-D monitoring network**
  - **Abandoned USTs**
  - **MTBE migration about 6,000 feet from source -- 1,500 feet further than benzene**
  - **Source depleted in MTBE**

  * Weaver *et al*., 1996

Contaminant Distribution 1995



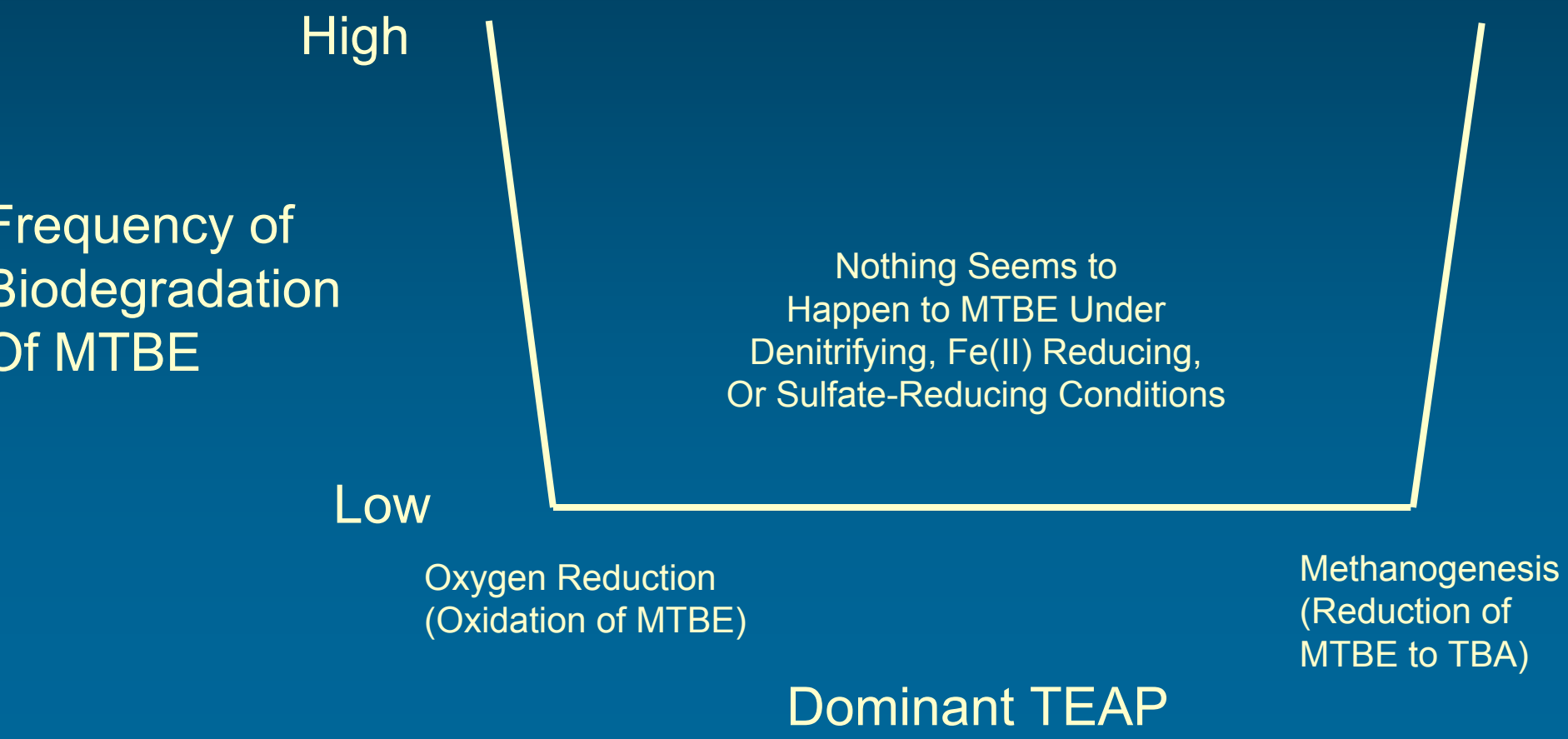


after Weaver *et al*., 1996

Biodegradation of MTBE

- Not well Documented (few case histories)
- Usually Slow when it does Occur
- Typically Occurs under Aerobic or Strongly Anaerobic (typically methanogenic) Conditions
- Under Aerobic Conditions “Oxidized”
- Under Strongly Anaerobic (methanogenic) Conditions “Reduced”

Susceptibility of MTBE to Biodegradation



MTBE Attenuation Processes

- **MTBE Seems to be Biologically Recalcitrant at Many Sites**
- **MTBE is generally not retarded, and moves with advective groundwater flow**
- **MTBE is not readily volatilized from water**
- **Therefore, *dispersion may be the predominant natural attenuation process***

Methods of Evaluating Natural Attenuation

- **Demonstrate loss of mass or reduction in concentration at field scale**
- **Spatial and temporal association of changing contaminant concentrations and geochemical indicators (O_2, NO_3^-, SO_4^{--}, Fe^{++}, CH_4)**
- **Direct microbiological evidence**

Considerations for Site Characterization

- **MTBE may be a constituent of any petroleum fuel**
- **MTBE may become rapidly depleted in source areas, but persist in downgradient areas**
- **MTBE migrates more rapidly, and to greater distances, than BTEX compounds**
- **MTBE and daughter products may not be detected at low concentrations, using certain analytical methods (SW8020/8021)**

Considerations for Site Characterization (continued)

- **Geochemical indicators of BTEX and MTBE biodegradation are the same -- MTBE biodegradation may be difficult to distinguish from BTEX biodegradation**

- **Principal anaerobic degradation product of MTBE (TBA) is also used as a fuel oxygenate -- its appearance is not conclusive evidence of biodegradation**

Recommendations

- **MTBE plumes and BTEX plumes may separate**
- **MTBE plumes may not stabilize at short distances from source**
- **Because of its Solubility, MTBE is Rapidly Depleted from the Source**
- **If Present, Monitoring locations should be selected with MTBE properties in mind**

Recommendations (continued)

- Use appropriate methods of chemical analyses [SW8260; DAI-GC/MS Method of Church *et al.* (1997)]
- Attempt to distinguish degradation from dispersion:
  - Mass balance/mass flux estimates
  - Use tracer to estimate site-specific value of dispersivity

Recommendations (concluded)

- **Properly-constructed microcosms may provide best site-specific evidence of MTBE biodegradation; may be time-consuming and expensive and certainly not something that AFCEE should undertake**